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ELECTRODEPOSITION OF NICKEL

Henry Brown, Huntington Woods, Mich., assignor to
The Udylite Corporation, Detroit, Mich., a corpora-
tion of Delaware

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This invention relates to the electrodeposition of nickel from an aqueous acidic bath.

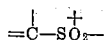
One object of this invention is to decrease the grain size and increase the luster of the nickel deposit.

A second and major object is the electrodeposition of brilliant, highly lustrous, ductile nickel plate.

It has been found that these objects can be accomplished by the use of certain organic compounds.

The first object mentioned above can be accomplished by the addition to the Watt's type of nickel bath or its modifications, of coumarin sulfonic acid. The presence of coumarin sulfonic acid in the bath causes the nickel plate which is electrodeposited therefrom to be very fine-grained (even though cloudy and milky in appearance), and to show marked increasing luster with continued plating.

It was further found that the second object, the production of brilliant, highly lustrous, ductile nickel plate, could be accomplished by the use, in conjunction with the coumarin sulfonic acid, of a material containing another different functional group, viz., the unsaturated methylene sulfone group,



as exemplified by benzene sulfonamides and sulfonimides. The presence of coumarin sulfonic acid alone in a Watt's type nickel bath or the presence of a material containing the unsaturated methylene sulfone group alone gives no obvious indication of the remarkably different and enhanced result which occurs when both materials are concurrently present.

While the simpler aryl sulfonamides and some of the aryl sulfonic acids produce bright and mirror-like deposits on buffed metals such as buffed brass, these compounds fail to accomplish the same result on steel which is polished, for example, with 200 emery paper or where the nickel is plated on top of matte (but unburnt) copper plate of 0.003" to 0.0005" thickness, and yield in these cases plate of dull and grey appearance. If, however, coumarin sulfonic acid and a material containing the unsaturated methylene sulfone group are used together, a brilliant mirror-like deposit can be obtained even on a matte copper deposit.

The aryl sulfones (sulfonamides, sulfonic acids), in general do not have a critical concentration range in the bath, and they produce practically no further improvement after their optimum concentration is reached. In the case of coumarin sulfonic acid, there is preferential reduction of the unsaturated compound with respect to the nickel ion, whereas with the aryl sulfones, the nickel ion is reduced preferentially. The variation of the reduction with the variation of the potentials between adjacent high and low points will account for the rate of brightening or "smoothing out" effect.

The uniqueness of the aryl sulfones, or broadly the



compounds, seems to be mainly tied up with the rate of reduction of the positive valent sulfur compound to negative valent sulfur compound, and the mechanism

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of its deposition. The fact that with α -naphthalene sulfonamide as the only organic compound in the bath, not only is the odor of naphthalene apparent at the cathode during the plating, but also the analysis of the plate shows the presence of carbon as well as sulfur and this indicates that the mechanism of the reduction is not of the simplest form.

It is not the sulfone group alone that is responsible for the effect of the aryl sulfones because the saturated alkyl sulfones are not nearly as effective as the aryl sulfones. The benzene and toluene sulfonamides and ortho benzoyl sulfonimide are more effective than aryl monosulfonic acids, especially of the benzene series, nevertheless, the latter, even though they may not produce bright plate on buffed metals, will give brilliant ductile plate when used in combination with coumarin sulfonic acid.

The concentration of coumarin sulfonic acid which may be advantageously employed is not critical in any concentration up to saturation and may be used at concentrations between about 0.5 gram per liter to about 3 grams/liter, the preferred concentration being 0.5 gram/liter to 2.0 grams/liter.

In keeping with their chemical activity, the higher the temperature of the bath, the more active are the unsaturated groups in the bath and smaller concentrations of compounds carrying them must be used. Furthermore, they function best at the higher pH values of the nickel bath, that is, 3.0 to 5.2, and their effectiveness in most cases drops rather suddenly when the pH is lowered past a certain value (in general, at a pH below 3.0 or 2.5, depending on the type of concentrated compound and on the temperature). The lower the temperature, the higher are the pH values that should be used, and conversely.

The best cathode film buffer is boric acid and it is important to keep its concentration high (over 30 grams/liter), especially in the warm baths. Other buffers may be used in small amounts (1 to 5 gram/liter) with the boric acid with beneficial effects, such as formic, citric, fluoboric acids, etc., but they are not recommended to be used alone.

In the use of coumarin sulfonic acid alone in the bath, or in the presence of the aryl sulfones, ammonium salts should be kept at a minimum. The concentration of zinc and copper ions in the bath should also be kept as low as possible. This is especially desirable where the concentration of aryl sulfones are low in the bath or the latter compounds are absent. A simple method for producing the coumarin sulfonic acid which is useful for the purposes of this invention, is to treat coumarin with a minimum of concentrated sulfuric acid to give a clear solution and this clear solution may be added directly to the bath.

The baths may be operated at pH values ranging from 2.0 to 5.5 and temperatures ranging from 20° C. to 70° C. and the preferred current density ranges may be from 5 to 150 amps./sq. ft. depending on the agitation, the temperature of the bath and the concentration and the type of nickel salts. The benzene sulfonamides and sulfonimides may be used effectively in concentrations of from 0.05 gram/liter to saturation.

In Table I are listed preferred bath compositions.

Table I

NiSO ₄ ·6H ₂ O, g./l.	NiCl ₂ ·6H ₂ O, g./l.	H ₃ BO ₃ , g./l.	Temp. (° C.)	Optimum pH
250-300	35-75	35-40	40-65	2.5-4.5
200-250	100-300	35-40	40-65	2.5-4.5
	75-100	35-40	40-65	2.5-4.5

In Table II are listed representative examples of the benzene sulfonamides and sulfonimides.

Table II

Benzene Sulfonamides and Sulfonimides	Optimum Conc., grams/liter
Benzene sulfonamide.....	0.1-3
Toluene sulfonamides.....	0.1-2
o-Benzoyl sulfimide.....	0.1-2
N-Benzoyl benzene sulfonimide.....	0.1-1
p-Toluene sulphonchloramide.....	0.1-1
p-Brom benzene sulfonamide.....	0.1-1
6-Chlor o-benzoyl sulfimide.....	0.1-1
M-Aldehydo benzene sulfonamide.....	0.1-1
Sulfomethyl benzene sulfonamide.....	0.1-6
Benzene sulfonamide m-carboxylic amide.....	0.1-3
7-Aldehydo o-benzoyl sulfimide.....	0.1-3
N-Acetyl benzene sulfonimide.....	0.1-2
Methoxy benzene sulfonamides.....	0.1-1
Hydroxymethyl benzene sulfonamide.....	0.1-2
p-Carboxylic amide benzene sulfonamide.....	0.1-3

Table III

Preferred formulations for use with the baths of Table I are as follows:

	Grams/liter
1. Coumarin sulfonic acid.....	0.5-2.0
2. Coumarin sulfonic acid.....	0.5-2.0
o-Benzoyl sulfimide.....	0.1-2
3. Coumarin sulfonic acid.....	0.5-2
Benzene sulfonamide.....	0.1-3

This application is a continuation-in-part of my prior application, Serial No. 749,344, filed May 20, 1947, which was itself a continuation-in-part of my prior application, Serial No. 366,385, filed November 20, 1940, both of which are now abandoned.

What is claimed is:

1. A bath for electrodepositing lustrous nickel comprising an aqueous acidic solution consisting essentially of an electrolyte selected from the group consisting of nickel sulfate, nickel chloride and a mixture of nickel sulfate and nickel chloride in the presence of 0.5 to 3.0 grams/liter of coumarin sulfonic acid.

2. A method for electrodepositing lustrous nickel con-

sisting of electrodepositing nickel from an aqueous acidic nickel solution consisting essentially of an electrolyte selected from the group consisting of nickel sulfate, nickel chloride and a mixture of nickel sulfate and nickel chloride in the presence of 0.5 to 3.0 grams/liter of coumarin sulfonic acid.

3. A method for electrodepositing bright nickel consisting of electrodepositing nickel from an aqueous acidic nickel solution consisting essentially of an electrolyte selected from the group consisting of nickel sulfate, nickel chloride, and a mixture of nickel sulfate and nickel chloride in the presence of an organic compound dissolved in the aqueous acidic nickel solution in a concentration falling within a range of about 0.05 gram/liter to saturation and selected from the group consisting of benzene sulfonamides and sulfonimides, said aqueous acidic nickel solution also having dissolved therein coumarin sulfonic acid in an amount of about 0.5 gram/liter to 3 grams/liter.

4. A bath for electrodepositing bright nickel comprising an aqueous acidic solution consisting essentially of an electrolyte selected from the group consisting of nickel sulfate, nickel chloride and a mixture of nickel sulfate and nickel chloride in the presence of an organic compound dissolved in the aqueous acidic nickel solution in a concentration of about 0.05 gram/liter to saturation and selected from the group consisting of benzene sulfonamides and sulfonimides, said aqueous acidic nickel solution also having dissolved therein coumarin sulfonic acid in an amount of about 0.5-3 grams per liter.

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